

U.S. ARMY MEDICAL RESEARCH INSTITUTE OF CHEMICAL DEFENSE

USAMRICD-TR-02-02

Proton Nuclear Magnetic Resonance Spectra of Sulfur Mustard and 2-Chlorotheyl ethyl Sulfide in Selected Solvents

Thomas P. Logan David A. Sartori

July 2002

20030321 098

Approved for public release; distribution unlimited

U.S. Army Medical Research Institute of Chemical Defense Aberdeen Proving Ground, MD 21010-5400

DISPOSITION INSTRUCTIONS:

Destroy this report when no longer needed. Do not return to the originator.

DISCLAIMERS:

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

The use of trade names does not constitute an official endorsement or approval of the use of such commercial hardware or software. This document may not be cited for purposes of advertisement.

A PERFORMING ORGANIZATION NAME(s) AND ADDRESS(ES) 1. REPORT DATE (SOUTH COME) 1. REPORT COME (SOUTH COME) 2. REPORT COME (SOUTH COME) 2. REPORT COME (SOUTH COME) 3. DATES COMERD (From COME) 5. GRANT NUMBER 5. WORK UNIT NUMBER 5. WORK UNIT NUMBER 5. WORK UNIT NUMBER 5. WORK UNIT NUMBER 5. AUTHOR(S) 1. STONE (SOUTH COME) 1. STONE (SOU	F	EPORT DO		Form Approved OMB No. 0704-0188						
The Burden Department of Outbrook withing the Department of Outbrook (Processing) 1715-1811-1811-1811-1811-1811-1811-1811-	Public reporting burden for this	collection of information is est	wing instructions, search	earching existing data sources, gathering and maintaining the						
May 2001 to June 2002 Article and Substitute Section Nuclear Magnetic Resonance Spectra of Sulfur Mustard and 2-Chloroethyl Ethyl	data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.									
4. HTILE AND SUBTITLE PROTOIN DUCIED WAS ABJUSTION OF SUBTOR MUSTARY AND ADDRESS (ES) Sulfide in Selected Solvents 5. CONTRACT NUMBER 5. PROGRAM ELEMENT NUMBER 5. PROGRAM ELEMENT NUMBER 5. PROGRAM ELEMENT NUMBER 5. PROGRAM ELEMENT NUMBER 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of National Proving Ground, MD Chemical Provin	•	, 1				· · · · · · · · · · · · · · · · · · ·				
Proton Nuclear Magnetic Resonance Spectra of Sulfur Mustard and 2-Chloroethyl Ethyl Sulfide in Selected Solvents 5. GRANT NUMBER 5. PROGRAM ELEMENT NUMBER 6. AUTHOR(S) 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER 8. PERFORMING ORGANIZATION REPORT NUMBER 9. PERFORMING ORGANIZATION REPORT NUMBER 10. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) 11. SPONSORIMONITOR'S ACRONYM(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Number(S) 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Number(S) 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Number(S) 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Number(S) 15. SUBJECT TERMS 16. SECURITY CLASSIFICATION OF: 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF PAGES UNICLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED 10. CRESS IN VARIETY OF PAGES UNICLASSIFIED UNCLASSIFIED UNCLASSIFIED 10. THE PAGE UNLASSIFIED UNCLASSIFIED OF PAGES UNICLASSIFIED UNCLASSIFIED UNCLASSIFIED 10. THE PAGE UNLASSIFIED UNCLASSIFIED OF THE PAGE UNICLASSIFIED OF THE PAGE UNICLASSIFIED OF THE PAGE UNICLASSIF			Technical Report							
Sulfide in Selected Solvents 6. AUTHOR(S) 6			atus of Culfus Massacad	Land O Chlamathad Ed		CONTRACT NUMBER				
Sc. PROGRAM ELEMENT NUMBER 62384 Sc. PROGRAM ELEMENT NUMBER 62384 Sc. PROJECT NUMBER 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 US Army Medical Research Institute Organization Organization Organization Organization O		•	ectra of Suffur Mustard	and 2-Chloroethyl El	-					
6. AUTHOR(S) Logan, T.P. and Sartori, D.A. 5. MORK UNIT NUMBER TC2 56. TASK NUMBER 51. WORK UNIT NUMBER TC2 56. TASK NUMBER 51. WORK UNIT NUMBER TO2 56. TASK NUMBER 51. WORK UNIT NUMBER TUSAMPLICE TRANSPORT NUMBER USAMPLICE TRANSPORT NUMBER 10. SPONSORMONITOR'S ACRONYM(S) 11. SPONSORMONITOR'S ACRONYM(S) 11. SPONSORMONITOR'S REPORT NUMBER(S) 11. SPONSORMONITOR'S REPORT NUMBER (S) 11. SPONSORMONITOR'S REPORT NUMBER(S) 11. SPONSORMONITOR'S REPORT NUMBER(S) 11. SPONSORMONITOR'S REPORT NUMBER(S) 11. SPONSORMONITOR'S REPORT NUMBER (S) 12. SPONSORMONITOR'S REPORT NUMBER (S) 13. SPONSORMONITOR'S REPORT NUMBER (S) AND	Sulfide in Selected S	Solvents			5b.	GRANT NUMBER				
Logan, T.P. and Sartori, D.A. TC2 56. TASK NUMBER 51. WORK UNIT NUMBER 52. PEPROFUNING ORGANIZATION REPORT NUMBER USAMRICD-TR-02-02 USAMRICD-TR-02-02 USAMRICD-TR-02-02 10. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) USATRY Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTY: MCMR-UV-RC 3100 Ricketts Point Road 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCL										
56. TASK NUMBER 57. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTN: MCMR-UV-DB 3100 Ricketts Point Road S. PERFORMING ORGANIZATION REPORT NUMBER USAMRICD-TR-02-02 USAMRICD-TR-02-02 USAMRICD-TR-02-02 10. SPONSOR/MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CES as well. In this study we used a 600 MHz MRM instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS 16. SUBJECT TERMS 17. LIMITATION OF ABSTRACT OF PAGES OF PAGES UNCLEASSIFIED UNCLASSIFIED OF PAGES OF The PAGE OF THE	6. AUTHOR(S) Logan T.P. and Sartori D.A.									
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTN: MCMR-UV-DB 3100 Rickets Point Road 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITORING AGENCY NAME(S) AND ADDRESS(ES) 11. SPONSOR/MONITOR'S AGRONYM(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES UNLIMITED 10. DID TELEPHONE NUMBER (include area code)		,			5e.	TASK NUMBER				
US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 8. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 10. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 11. SPONSOR/MONITOR'S ACRONYM(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 16. SUBJECT TERMS 19. NUMBER UNCLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 19. NAME OF RESPONSIBLE PERSON Thomas P. Logan 190. TELEPHONE NUMBER (include area code)			5f. \	5f. WORK UNIT NUMBER						
US Army Medical Research Institute of Chemical Defense 21010-5400 Aberdeen Proving Ground, MD 21010-5400 US AMRICD-TR-02-02 US AMRICD-TR-02-02 US Amry Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 S. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS Sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF ABSTRACT OF ABSTRACT UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED 10. LEEPHONE NUMBER (include area continuing interest in the analysis of sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFIED UNCLASSIFIED 10. SECURITY C	7. PERFORMING ORG	ANIZATION NAME(S)	AND ADDRESS(ES)							
Chemical Defense 3100 Ricketts Point Road 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 11. SPONSOR/MONITORIS ACRONYM(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-thoroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz MMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 16. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT	TIO A Madical D		Abandaan Duasi	and Comment MD	, n	IUMBER				
ATTN: MCMR-UV-DB 3100 Ricketts Point Road 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD 21010-5400 11. SPONSOR/MONITOR'S ACRONYM(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for Din a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES ONLINIMITED UNILLASSIFIED UNILLIMITED UNILLASSIFIED UNILLASSIFIED UNILLASSIFIED UNILLASSIFIED UNILLASSIFIED UNILLIMITED (DIA) 10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'	-	esearch institute of		ing Ground, MD	110	AMDICD TD 02 02				
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz MRR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES OF PAGE		-DR	21010-3400		03	AWRICD-TR-02-02				
B. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Army Medical Research Institute of Aberdeen Proving Ground, MD Chemical Defense 21010-5400 ATTN: McMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED 10. ABSTRACT OF PAGES 11. SPONSOR/MONITOR'S ACRONYM(S) 12. NAMBER(S) 11. SPONSOR/MONITOR'S ACRONYM(S)										
US Army Medical Research Institute of 21010-5400 Chemical Defense 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF ABSTRACT OF AGES Thomas P. Logan 19. TELEPHONE NUMBER (include area code) 19. TELEPHONE NUMBER (include area code)	order residents and residents	1040								
US Army Medical Research Institute of 21010-5400 Chemical Defense 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF ABSTRACT OF AGES Thomas P. Logan 19. TELEPHONE NUMBER (include area code) 19. TELEPHONE NUMBER (include area code)	9. SPONSORING / MC	NITORING AGENCY I	NAME(S) AND ADDRESS	S(ES)	10.	SPONSOR/MONITOR'S ACRONYM(S)				
Chemical Defense 21010-5400 ATTN: MCMR-UV-RC 3100 Ricketts Point Road 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 11. SPONSOR/MONITOR'S 11. SPONSOR/MONITOR'S 11. SPONSOR MAN AND AND AND AND AND AND AND AND AND A										
NUMBER(S) 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents. 16. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents. 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES OF	Chemical Defense			,						
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	ATTN: MCMR-UV	-RC			11.	SPONSOR/MONITOR'S REPORT				
Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (MMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES OF PAGES UNCLASSIFIED un						NUMBER(S)				
Approved for public release; distribution unlimited 13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (MMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES OF PAGES UNCLASSIFIED un										
13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19a. NAME OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	12. DISTRIBUTION / A	VAILABILITY STATE	MENT							
13. SUPPLEMENTARY NOTES 14. ABSTRACT Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19a. NAME OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	Approved for public	release; distribution	unlimited							
Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	13. SUPPLEMENTAR	NOTES								
Our laboratory has a continuing interest in the analysis of sulfur mustard (HD) for the purpose of developing medical countermeasures. Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
Nuclear magnetic resonance (NMR) spectroscopy is an important analytical technique for studying HD chemistry in simple solutions and in complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	14. ABSTRACT									
complex matrices. To support research in this area, we have developed a list of proton assignments for HD in a variety of suitable solvents. Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	Our laboratory has a	continuing interest	in the analysis of sulfu	r mustard (HD) for the	e purpose of de	veloping medical countermeasures.				
Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19a. NAME OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents. These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
These results can assist researchers in identifying HD and CEES in variety of solvents. 15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	Because the half mustard 2-chloroethyl ethyl sulfide (CEES) is a non-surety analogue of HD we have added a list of proton assignments for									
15. SUBJECT TERMS sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	CEES as well. In this study we used a 600 MHz NMR instrument to investigate 2-mM solutions of HD and CEES in deuterated solvents.									
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	These results can assist researchers in identifying HD and CEES in variety of solvents.									
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)				,						
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)										
16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF ABSTRACT OF PAGES 18. NUMBER OF RESPONSIBLE PERSON Thomas P. Logan 19b. TELEPHONE NUMBER (include area code)	15. SUBJECT TERMS									
a. REPORT b. ABSTRACT c. THIS PAGE UNLIMITED 10 Telephone NUMBER (include area code)	sulfur mustard (HD), chloroethylethylsulfide (CEES), proton nuclear magnetic spectroscopy, 2 mM solutions, deuterated solvents									
a. REPORT b. ABSTRACT c. THIS PAGE UNLIMITED 19b. TELEPHONE NUMBER (include area unclassified un	16. SECURITY CLASSIFICATION OF:									
UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED 10 code)	• DEDODT	h ADSTDACT	A THIS DAGE		J					
	UNCLASSIFIED			UNLIMITED	10	code)				

Introduction

Sulfur mustard (HD) is a vesicating chemical warfare agent that has been investigated by our laboratory for the express purpose of developing medical countermeasures. Solutions of HD are prepared in a variety of solvents to aid researchers. In these investigations nuclear magnetic resonance (NMR) spectroscopy has been playing a larger roll in the analysis and study of HD. 1,2,3 In a recent work we measured the half-life of HD in D_2O . This study required a demonstration of proton NMR spectral assignments for HD in D_2O because previous studies 5,6 indicated that solution of HD in aqueous media was followed instantaneously by hydrolysis. We verified the presence of HD by preparing 2-mM solutions of HD in D_2O containing 0.17 M NaCl. Five minutes after preparation of the solution, HD was extracted with deuterated hexane, and we demonstrated that the HD extracted had the same proton NMR spectra as a direct preparation of HD in deuterated hexane. The changes in the chemical shifts of HD in D_2O versus HD in deuterated hexane prompted us to undertake this study of HD and 2-chloroethyl ethyl sulfide (CEES) in a variety of available deuterated solvents.

We prepared 2-mM solutions of HD in nine solvents and 2-mM solutions of CEES in eight solvents. The proton spectra for each of these solutions demonstrate the changes that occur when HD and CEES respectively are placed in different solvents.

Materials and Methods

The sulfur mustard (2,2'-dichlorodiethyl sulfide, HD) employed in this study was obtained from the US Army Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD). The purity was 97.5% as determined by NMR spectroscopy. 2-chloroethyl ethyl sulfide (CEES, 98%), deuterated solvents (99+%), and 3-(trimethylsilyl)-1-propanesulfonic acid-d₄ were obtained from Sigma-Aldrich and used as received.

¹H NMR analysis

A previously prepared and frozen sample of 2 mM HD in D_2O was thawed to room temperature and thoroughly mixed by vortexing for three minutes. For the other solvents used in this work, 2-mM preparations were prepared volumetrically and stored at -70 °C. A 500 μ L aliquot of the solution was transferred into 5-mm o.d. NMR tubes. All data were collected on a Varian Unity Inova 600 MHz NMR spectrometer using the standard ¹H pulse sequence. The WET pulse sequence for solvent suppression was utilized for the D_2O sample. Probe temperature was calibrated to 22.0 \pm 0.1 °C by standard means. Samples were referenced to residual proto-solvent peaks. The D_2O sample was referenced to 3-(trimethylsilyl)-1-propanesulfonic acid-d₄ at 0 ppm.

Results

Tables 1 and 2 list chemical shift and coupling constants for HD and CEES in the various solvents studied. Figure 1 shows the number scheme used for the protons in the tables.

Figure 1. Structures of HD and CEES and numbering scheme for the protons of HD and CEES.

CI
$$\frac{2}{1}$$
 S $\frac{2}{1}$ CI $\frac{3}{4}$ S $\frac{1}{2}$ CI $\frac{2}{2}$ 2,2'-chloroethyl sulfide (HD) 2-chloroethyl ethyl sulfide

Table 1. Chemical shift (ppm) and coupling constants (Hz) for HD in various solvents

Solvent	H ^{2,2'}	H ^{1,1'}	
CDCI ₃	3.65 (7.6)	2.92 (7.6)	
CD₃CN	3.71 (7.6)	2.92 (7.6)	
CD ₃ C(O)CD ₃	3.75 (7.6)	2.98 (7.6)	
CD ₂ Cl ₂	3.66 (7.6)	2.92 (7.6)	
CD ₃ S(O)CD ₃	3.76 (7.6)	2.92 (7.6)	
C ₂ D ₅ OD	3.66 (7.6)	2.92 (7.6)	
C ₃ D ₇ OD	3.70 (7.6)	2.96 (7.6)	
C_6D_{14}	3.60 (8.2)	2.92 (7.6)	
D ₂ O ⁽⁴⁾	3.74 (7.6)	3.00 (7.6)	

Table 2. Chemical shift (ppm) and coupling constants (Hz) for CEES in various solvents.

Solvent	H ²	H ¹	H ³	H⁴
CDCI ₃	3.64 (7.6)	2.87 (7.6)	2.61 (7.6)	1.28 (7.6)
CD₃CN	3.69 (7.6)	2.87 (7.6)	2.60 (7.6)	1.23 (7.6)
CD ₃ C(O)CD ₃	3.70 (7.6)	2.87 (7.6)	2.62 (7.6)	1.23 (7.6)
CD ₂ Cl ₂	3.64 (7.6)	2.86 (7.6)	2.59 (7.6)	1.26 (7.6)
CD ₃ S(O)CD ₃	3.73 (7.6)	2.84 (7.6)	2.58 (7.6)	1.16 (7.6)
C ₂ D ₅ OD	3.62 (7.6)	2.83 (7.6)	2.59 (7.6)	1.24 (7.6)
C ₃ D ₇ OD	3.65 (7.6)	2.87 (7.6)	2.64 (7.6)	1.30 (7.6)
C ₆ D ₁₄	3.59 (8.2)	2.87 (7.6)	2.63 (7.6)	а

a. Peak obscured by methyl groups in solvent.

Discussion

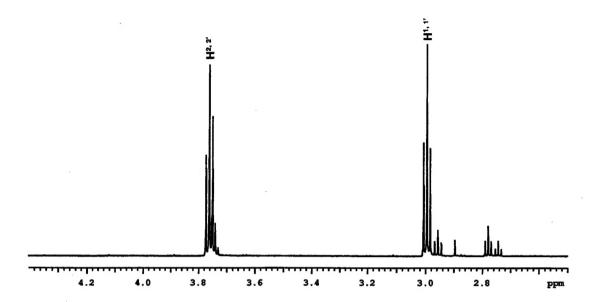
The influence of solvent on chemical shift for HD is relatively small (Table 1). For methylene protons $H^{1,1'}$, beta to the chloride, the greatest downfield change occurs in D_2O at 3.00 ppm. This can be attributed, at least in part, to the large dielectric constant of D_2O . HD has limited solubility⁸ in and reacts with D_2O to form deuterated thiodiglylcol (TDG).^{4,8} In Figure 2, assignments for HD in D_2O are as follows: a region of overlapping methylene peaks for -CH₂-Cl in HD and -CH₂-OH in (TDG) at 3.7-3.8 ppm, methylene peaks for -S-CH₂ in HD at 3.00 ppm; peaks related to the reaction intermediate chlorohydrin at 2.96 and 2.78 ppm; 1,4 dithiane impurity at 2.90 ppm; and methylene peaks for -S-CH₂ in TDG at 2.74 ppm.

HD is much more stable in the remaining solvents in Table 1 than in D_2O . Figure 3 demonstrates this stability of HD in hexane. This stability gives the researcher a range of solvent choices to study HD. For methylene protons $H^{2,2}$, alpha to the chloride, in HD there is a slightly larger influence of solvent on chemical shift.

The chemical shifts for CEES in Table 2 show little solvent influence. H¹ and H² chemical shifts for the one-armed mustard CEES are located near H^{1,1'} and H^{2,2'} values

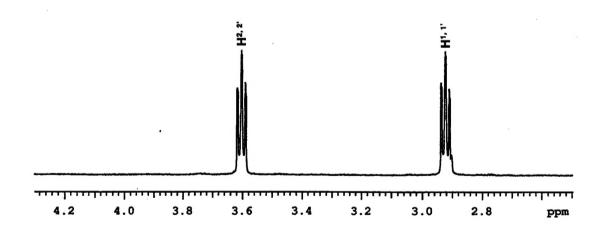
for HD, and this is expected based on the similar molecular environment for these methylene protons in CEES and HD (Figure 1). The remaining methylene protons H³ and methyl protons H⁴ are at 2.6 ppm and 1.2-1.3 ppm respectively. Representative proton NMR spectra are shown for CEES in deuterated chloroform, Figures 4, and deuterated acetonitrile, Figure 5. The additional peaks in these figures are due to water and non-deuterated solvent impurities. These data provide a reference source for the proton NMR chemical shifts of CEES and HD in the solvents studied.

Figure 2. HD in D₂O, containing 0.17 M NaCl, approximately 15 min. after preparation



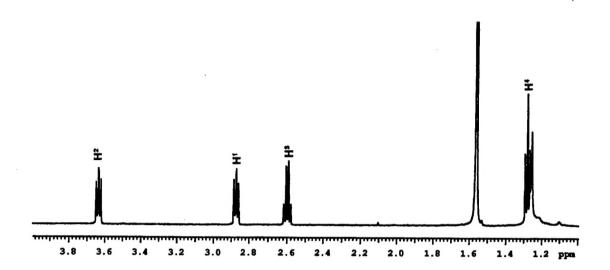
Proton NMR of HD and solvolysis products of HD in D₂O, containing 0.17 M NaCl, approximately 15 min after thawing and vortexing a 2 mM preparation.

Figure 3. HD in deuterated hexane



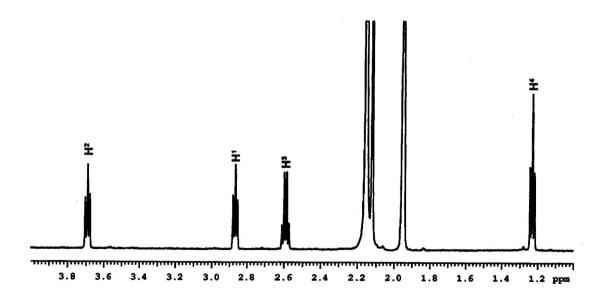
HD in deuterated hexane after extraction from HD in D_2O containing 0.17 M NaCl.

Figure 4. CEES in deuterated chloroform



CEES in deuterated chloroform at 2 mM; peaks in addition to those listed in Table 2 are due to water and non-deuterated solvent impurities.

Figure 5. CEES in deuterated acetonitrile



CEES in deuterated acetonitrile at 2mM; peaks in addition to those listed in Table 2 are due to water and non-deuterated solvent impurities.

References

1. Arroyo C.M., Schafer R.J., and Carmichael A.J. (2000) Reactivity of chloroethyl sulfides in the presence of a chlorinated prophylactic: A kinetic study by EPR/spin trapping and NMR techniques. Journal of Applied Toxicology 20, 7-12.

2. Shih M.L., Korte W.D., Smith J.R., and Szafraniec L.L. (1999) Reactions of Sulfides with S-330, a Potential Decontaminant of Sulfur Mustard in Formulations. Journal of

Applied Toxicology 19, S83-S88.

3. Shih M.L., Korte W.D., Smith J.R., and Szafraniec L.L. (1999) Analysis and Stability of the Candidate Sulfur Mustard Decontaminant S-330. Journal of Applied Toxicology 19, S89- S95.

4. Logan T.P. and Sartori D.A. (2001) Nuclear Magnetic Resonance Analysis of the Solution and Solvolysis of Sulfur Mustard in D₂O submitted to Toxicology Methods.

- Yang Y.-C., Szafraniec L.L., Beaudry W.T., Ward J.R. (1988) Kinetics and Mechanism of the Hydrolysis of 2-Chloroethyl Sulfides. J. Org. Chem. 53, 3293-3297.
- Yang Y.-C., L.I. Szafraniec L.L., Beaudry W.T., Ward J.R. (1987) Direct NMR Measurements of Sulfonium Chlorides Produced from the Hydrolysis of 2-Chloroethyl sulfides. J. Org. Chem. 52,1637-1638.
- 7. Smallcombe S.H., Patt S.L., Keifer P.A. (1995) WET Solvent Suppression and Its Applications to LC NMR and High-Resolution NMR Spectroscopy. J. Magn. Res. A117, 295-303.
- 8. Papirmeister B., Feister A.J., Robinson S.I., and Ford R.D. (1991) Medical Defense Against Mustard Gas: Toxic Mechanisms and Pharmacological Implications, Toxicodynamics of Sulfur Mustard, 92, CRC Press, Boca Raton, FL.